5.10 Total Alkalinity

What is total alkalinity and why is it important?

Alkalinity is a measure of the capacity of water to neutralize acids (see pH description). Alkaline compounds in the water such as bicarbonates (baking soda is one type), carbonates, and hydroxides remove H+ ions and lower the acidity of the water (which means increased pH). They usually do this by combining with the H+ ions to make new compounds. Without this acid-neutralizing capacity, any acid added to a stream would cause an immediate change in the pH. Measuring alkalinity is important in determining a stream's ability to neutralize acidic pollution from rainfall or wastewater. It's one of the best measures of the sensitivity of the stream to acid inputs.

Alkalinity in streams is influenced by rocks and soils, salts, certain plant activities, and certain industrial wastewater discharges.

Total alkalinity is measured by measuring the amount of acid (e.g., sulfuric acid) needed to bring the sample to a pH of 4.2. At this pH all the alkaline compounds in the sample are "used up." The result is reported as milligrams per liter of calcium carbonate (mg/L $CaCO_3$).

Analytical ana equipment considerations

For total alkalinity, a double endpoint titration using a pH meter (or pH "pocket pal") and a digital titrator or buret is recommended. This can be done in the field or in the lab. If you will analyze alkalinity in the field, it is recommended that you use a digital titrator instead of a buret because the buret is fragile and more difficult to set up and use in the field. The alkalinity method described below was developed by the Acid Rain Monitoring Project of the University of Massachusetts Water Resources Research Center.

Burets, titrators, and digital titrators for measuring alkalinity

The total alkalinity analysis involves titration. In this test, titration is the addition of small, precise quantities of sulfuric acid (the reagent) to the sample until the sample reaches a certain pH (known as an endpoint). The amount of acid used corresponds to the total alkalinity of the sample. Alkalinity can be measured using a buret, titrator, or digital titrator (described below).

- A *buret* is a long, graduated glass tube with a tapered tip like a pipet and a valve that is opened to allow the reagent to drip out of the tube. The amount of reagent used is calculated by subtracting the original volume in the buret from the volume left after the endpoint has been reached. Alkalinity is calculated based on the amount used.
- *Titrators* forcefully expel the reagent by using a manual or mechanical plunger. The amount of reagent used is calculated by subtracting the original volume in the titrator from the volume left after the endpoint has been reached. Alkalinity is then calculated based on the amount used or is read directly from the titrator.
- *Digital titrators* have counters that display numbers. A plunger is forced into a cartridge containing the reagent by turning a knob on the titrator. As the knob turns, the counter changes in proportion to the amount of reagent used. Alkalinity is then calculated based on the amount used. Digital titrators cost approximately $90.

Digital titrators and burets allow for much more precision and uniformity in the amount of titrant that is used.

How to collect and analyze samples

The field procedures for collecting and analyzing samples for pH and total alkalinity consist of the following tasks:

TASK 1 **Prepare the sample containers**

Sample containers (and all glassware used in this procedure) must be cleaned and rinsed before the first run and after each sampling run by following the procedure described under Method A on page 128. Remember to wear latex gloves.

TASK 2 **Prepare before leaving for the sampling site**

Refer to pages 19-21 for details on confirming sampling date and time, safety considerations, checking supplies, and checking weather and directions. In addition to the standard sampling equipment and apparel, when sampling for pH and alkalinity include the following equipment:

- Digital titrator
- 100-mL graduated cylinder
- 250-mL beaker
- pH meter with combination temperature and reference electrode or pH "pocket pal"
- Sulfuric acid titration cartridge, 0.16 N
- Data sheet for pH and total alkalinity to record results
- Alkalinity voluette ampules standard, 0.500 N, for accuracy check
- Wash bottle with deionized water to rinse pH meter electrode
- Magnetic stirrer, if titrated in the lab

Be sure to calibrate the pH meter before you analyze a sample. The pH meter should be calibrated prior to sample analysis and after every 25 samples according to the instructions in the meter manual. Use two pH standard buffer solutions: 4.01 and 7.0. Following are notes regarding buffers:

- The buffer solutions should be at room temperature when you calibrate the meter.
- Do not use a buffer after its expiration date.
- Always cap the buffers during storage to prevent contamination.
- Because buffer pH values change with temperature, the meter must have a built-in temperature sensor that automatically standardizes the pH when the meter is calibrated.
- Do not reuse buffer solutions!

Be sure to let someone know where you are going and when you expect to return.

TASK 3 **Collect the sample**

Refer to page 128 for details on how to collect water samples using screw-cap bottles or Whirl-pak® bags.

TASK 4 **Measure total alkalinity (field or lab)**

The following steps are for use of a digital titrator in the field or the lab. If you are using a buret, consult Standard Methods (APHA, 1992).

Alkalinity is usually measured using sulfuric acid with a digital titrator. Sulfuric acid is added to the water sample in measured amounts until the three main forms of alkalinity (bicarbonate, carbonate, and hydroxide) are converted to carbonic acid. At pH 10, hydroxide (if present) reacts to form water. At pH 8.3, carbonate is converted to bicarbonate. At pH 4.5, it is certain that all carbonate and bicarbonate are converted to carbonic acid. Below this pH, the water is unable to neutralize the sulfuric acid and there is a linear relationship between the amount of sulfuric acid added to the sample and the change in the pH of the sample. So, additional sulfuric acid is added to the sample to reduce the pH of 4.5 by exactly 0.3 pH units (which corresponds to an exact doubling of the pH) to a pH of 4.2. However, the exact pH at which the conversion of these bases might have happened, or total alkalinity, is still unknown. This procedure uses an equation derived from the slope of the line described above to extrapolate back to the amount of sulfuric acid that was added to actually convert all the bases to carbonic acid. The multiplier (0.1) then converts this to total alkalinity as mg/L $CaCO_3$. The following steps outline the procedures necessary to determine the alkalinity of your sample.

1. Insert a clean delivery tube into the 0.16 N sulfuric acid titration cartridge and attach the cartridge to the titrator body.
2. Hold the titrator, with the cartridge tip pointing up, over a sink. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to 0 and wipe the tip.
3. Measure the pH of the sample (see pH, section, 5.4). If it is less than 4.5, go to step 9 below.
4. Insert the delivery tube into the beaker containing the sample. Turn the delivery knob while magnetically stirring the beaker until the pH meter reads 4.5. Record the number of digits used to achieve this pH. Do not reset the counter.
5. Continue titrating to a pH of 4.2 and record the number of digits.
6. Apply the following equation:

Alkalinity (as mg/L $CaCO_3$) = (2a - b) x 0.1

Where:

a = digits of titrant to reach pH 4.5
b = digits of titrant to reach pH 4.2 (including digits required to get to pH 4.5)
0.1 = digit multiplier for a 0.16 titration cartridge and a 100-mL sample

Example:

Initial pH of sample is 6.5.
It takes 108 turns to get to a pH of 4.5.
It takes another 5 turns to get to pH 4.2, for a total of 113 turns.
Alkalinity = ((2 x 108) - 113) x 0.1
= 10.3 mg/L

7. Record the results as mg/L alkalinity on the lab sheet.
8. Rinse the beaker with distilled water before the next sample.
9. If the pH of your water sample, prior to titration, is less than 4.5, proceed as follows:
   - Insert the delivery tube into the beaker containing the sample.
   - Turn the delivery knob while swirling the beaker until the pH meter reads exactly 0.3 pH units less than the initial pH of the sample.
   - Record the number of digits used to achieve this pH.
   - Apply the equation as in step 6, but a = 0 and b = the number of digits required to reduce the initial pH exactly 0.3 pH units.

Example:

Initial pH of sample is 4.3.
Enter "0" in the 4.5 column on the lab sheet.
Titrate to a pH of 0.3 units less than the initial pH—in this case 4.0.
It takes 10 digits to get to 4.0.
Enter this in the 4.2 column on the lab sheet and note that the pH endpoint is 4.0.
Alkalinity = (0 - 10) x 0.1 = -1.0.

- Record the results as mg/L alkalinity on the lab sheet.

10. Perform an accuracy check on the first field sample, halfway through the run, and after analysis of the last sample as described below. Check the pH meter against pH 7.0 and 4.01 buffers after every 10 samples.

TASK 5 **Perform an accuracy check**

This accuracy check should be performed on the first field sample titrated, again about halfway through the field samples, and at the final field sample.

1. Snap the neck off an alkalinity voluette ampule standard, 0.500 N. Or if using a standard solution from a bottle, pour a few milliliters of the standard into a clean beaker.
2. Pipet 0.1 mL of the standard to the titrated sample (see above). Resume titration back to the pH 4.2 endpoint. Record the number of digits needed.
3. Repeat using two more additions of 0.1 mL of standard. Titrate to the pH 4.2 after each addition.
4. Each 0.1-mL addition of standard should require 250 additional digits of 0.16 N titrant.

TASK 6 **Return the field data sheets and samples to the lab or drop-off point**

Alkalinity samples must be analyzed within 24 hours of their collection. If the samples cannot be analyzed in the field, keep the samples on ice and take them to the lab or drop-off point as soon as possible.

References

APHA. 1992. *Standard methods for the examination of water and wastewater.* 18th ed. American Public Health Association, Washington, DC.

Godfrey, P.J. 1988. *Acid rain in Massachusetts.* University of Massachusetts Water Resources Research Center, Amherst, MA.

River Watch Network. 1992. *Total alkalinity and pH field and laboratory procedures* (based on University of Massachusetts Acid Rain Monitoring Project). July 1.